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(54) PRODUCTION OF 1,1-DIHALO-4-METHYL PENTADIENES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to the preparation of chemical intermediates useful in the preparation of insecticides.

2-(2,2-Dichlorovinyl)-3,3-dimethylcyclopropane carboxylic acid is an important intermediate in the production of insecticides, including, for example, 3-phenoxybenzyl-2-(2,2-dichlorovinyl)-3,3-dimethylcyclo propane carboxylate. The preparation of the acid from 1,1-dichloro-4-methyl-1,3-pentadiene is described by Farkas *et al* (Collection Czechoslovak Chem. Comm., (1959) *24* pp. 2230-2236). However, the preparation of the pentadiene derivative was achieved by a cumbersome four-stage process.

In our co-pending British Patent Application No. 27923/75 (Serial No. 1531733) we describe a much simpler process for the preparation of 1,1-dichloro-4-methyl-1,3-pentadiene in which isobutene is contacted with a 1,1,2-trihaloethylene in gas phase at elevated temperature. We have now found that the same reaction may be performed in liquid phase.

According to the present invention, a process for the production of 1,1-dihalo-4-methyl-1,3-pentadiene comprises the step of contacting isobutene with a 1,1,2-trihaloethylene in liquid phase, optionally in the presence of an inert solvent of suitable critical temperature, at a temperature in the range 125°C to the critical temperature of the liquid phase, and subsequently isomerising any 1,1-dihalo-4-methyl-1,4-pentadiene produced to the 1,3 isomer.

The principal product of the reaction is either a 1,1-dihalo-4-methyl-1,3-pentadiene (A) an isomeric 1,1-dihalo-4-methyl-1,4-pentadiene (B), or a mixture of the two isomers, depending on the temperature of the reaction. For example, at 260°C only isomer (A) is produced whereas at 150°C only isomer (B) is found, and at 200°C the product comprises a mixture of isomers (A) and (B). In each case some 2,5-dimethylhexa-1,5-diene is also produced, its proportion generally increasing with increasing reaction temperature. Since the desired product of the reaction is isomer (A), if only isomer (B) or a mixture of (A) and (B) is obtained, the product must be isomerised to isomer (A). This may be achieved by heating with a suitable isomerisation catalyst. An especially effective method comprises heating the product with a trace of *p*-toluene sulphonic acid at a temperature in the range 100-170°C. It is preferred that the reaction temperature is at least 200°C.

By the term "halo" we particularly intend the chloro and bromo derivatives. Thus the reaction is especially directed to the production of 1,1-dibromo-4-methyl-1,3-pentadiene and 1,1-dichloro-4-methyl-1,3-pentadiene.

Suitable 1,1,2-trihaloethylenes for use in the process of our invention include trichloroethylene and tribromoethylene, but mixed halo compounds may be used, for example, 1,1-dichloro-2-bromoethylene. If desired a mixture of trihaloethylenes may be used.

In order that the reaction may be conducted in the liquid phase, it is essential that the temperature of the reaction does not exceed the critical temperature of the liquid phase. When no solvent is used this corresponds to the critical temperature of the halo compound used; but when a solvent is used it is the critical temperature of the solution of halo compound in the solvent. For example, when trichloroethylene is used without solvent the critical temperature is 271°C, so that the reaction is normally conducted at a temperature of 260°C, but when tetradecane is used as solvent a reaction temperature of 300°C may be used. The solvent used must be inert to both reactants and products and have a critical temperature greater than the reaction temperature.

Hydrocarbon solvents are preferred, for example, tetradecane.

The reaction is most conveniently carried out batchwise in an autoclave under autogenous pressure, although it may be carried out on a continuous basis, provided that the pressure is sufficient to maintain liquid phase operation. The products from the autoclave or effluent from a continuous reactor may be readily separated, e.g. by distillation the unreacted starting materials being recovered and recycled. When isomer (B) or a mixture of isomers (A) and (B) is obtained the necessary isomerisation step may be carried out before or after the separation step.

The reaction may be conducted in the presence of free-radical initiators, e.g. peroxides such as *t*-butylhydroperoxide, especially when temperatures at the lower end of the range are used. Alternatively, ionising radiations may be used to facilitate reaction.

The invention is illustrated by the following Examples:

Examples 1-5

Trichloroethylene (575 m mole) and tertiary butyl hydroperoxide (5 g) were placed in a 230 ml stainless steel autoclave. The autoclave was flushed with nitrogen, sealed and charged with isobutene (287.5 m mole). The temperature was increased to X°C during a 25 min. period and maintained at that temperature for a further 1 hour. During reaction the autoclave was rocked to ensure adequate mixing. After cooling and venting, the reaction mixture was analysed by gas/liquid chromatography (GLC), using a 2 metre $\beta\beta'$ oxy di-propionitrile column at 70°C under a nitrogen flow equivalent to 10 psig.

The results are set out in Table 1 below. The % conversion shown against each product is calculated on trichloroethylene initially present.

Table

Reaction temperature (X°C)	1,1'dichloro-4-methyl-penta-1,3-diene Isomer (A)		1,1'dichloro-4-methyl-penta-1,4-diene (Isomer (B)		2,5 dimethylhexa-1,5-diene
	m mole	% Conversion	m mole	% Conversion	m mole
125	nil	nil	0.63	0.11	0.1
150	nil	nil	1.84	0.32	0.86
175	nil	nil	2.3	0.4	0.8
200	2.06	0.36	1.51	0.26	1.99
260	9.7	1.7	nil	nil	3.52

When the procedure was repeated at a temperature of 110°C there was no measurable reaction.

Example 6

Trichloroethylene (241 m mole) and tetradecane (25 ml) were placed in a 230 ml stainless steel autoclave. The autoclave was sealed and charged with isobutene (56 m mole) and the temperature increased to 300°C over a 25 minute period and maintained at this temperature for 1 hour. During reaction the autoclave was rocked to ensure adequate mixing. After cooling and venting, the reaction mixture was subjected to GLC analysis as for Example 1. The reaction products were:-

1,1-dichloro-4-methylpenta-1,3-diene: 0.9 m mole 1.6% conversion
2,5-dimethylhexa-1,5-diene: 3.6 m mole

WHAT WE CLAIM IS:-

1. Process for the production of 1,1-dihalo-4-methyl-1,3-pentadiene which comprises the step of contacting isobutene with a 1,1,2-trihaloethylene in liquid phase optionally in the presence of an inert solvent of suitable critical temperature at a temperature in the range 125°C up to the critical temperature of the liquid phase, and subsequently isomerising any 1,1-dihalo-4-methyl-1,4-pentadiene produced to the 1,3 isomer.

2. Process according to claim 1 in which the trihalo-ethylene is 1,1,2-trichloroethylene.

3. Process according to claim 1 or claim 2 in which the reaction is carried out at a temperature of at least 200°C.

4. Process according to claim 1 in which the said isomerisation is carried out by heating in the presence of p-toluene sulphonic acid.

5. Process according to claim 1 or claim 2 in which the reaction temperature is chosen so as to maximise the proportion of the 1,1-dihalo-4-methylpentadiene which is present as the 1,3 isomer.

6. Process according to any one of claims 1 to 5 in which a free-radical initiator is added to the reaction mixture.

7. Process for the production of a 1,1-dihalo-4-methyl-1,3 pentadiene according to claim 1 and substantially as described in any one of Examples 1 to 6.

8. 1,1-Dichloro-4-methyl-1,3-pentadiene whenever prepared by a process according to any one

of claims 1 to 7.

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